February 21, 2010

Via E-Mail: dmcclure@waterboards.ca.gov

Mr. Daniel McClure, P.E.
Water Resource Control Engineer/Project Manager
TMDL Unit
Central Valley Regional Water Quality Control Board (CVWRQCB)
11020 Sun Center Dr. #200
Rancho Cordova, CA 95670

Subject:	**Comments on Draft Water Quality Criteria Document for Lambda-Cyhalothrin**

Dear Mr. McClure:

On behalf of Syngenta Crop Protection, Inc., I am submitting comments (Appendix 1) on the recently released draft report on Lambda-Cyhalothrin Criteria Derivation ([1]Fojut and Tjeerdema, 2010). Syngenta is the primary registrant for lambda-cyhalothrin and requests that these comments be considered and addressed in the final lambda-cyhalothrin WQC guidance document.

Please contact Debbie Stubbs, Syngenta Regulatory Affairs, at 336-632-2449 or debbie.stubbs@syngenta.com if you have any questions regarding these comments. Thank you in advance for your consideration.

Sincerely,

(Original signed by KSH)

Kevin S. Henry, Ph.D.
Environmental Toxicologist

[1] Fojut, T.L. and Tjeerdema, R.S. 2010. Lambda-Cyhalothrin Criteria Derivation DRAFT. Posted at: http://www.waterboards.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/central_valley_pesticides/criteria_method/index.sht

Appendix 1. Comments on “Lambda-Cyhalothrin Criteria Derivation Draft”

Comments on Draft Water Quality Criteria Report for Lambda-Cyhalothrin Issued by the California Regional Water Quality Control Board, Central Valley

by
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CSI Report No. 10709

February 19, 2010

Summary

A draft water quality criteria report for the pyrethroid insecticide lambda-cyhalothrin has been issued by the University of California, Davis (UCD) and is being circulated for public comment. Compliance Services International (CSI), Lakewood WA, has developed the comments presented herein on behalf of Syngenta Crop Protection, Inc., the registrant for lambda-cyhalothrin. These comments address four main areas: derivation of Acute and Chronic Criteria; aspects of the UCD methodology; bioavailability; and mesocosm and microcosm data.

Criteria Derivation for Lambda-Cyhalothrin: CSI examined the data selected by UCD for derivation of the acute and chronic criteria for lambda-cyhalothrin and found it to be generally consistent with the data compiled by the Pyrethroid Working Group, of which Syngenta is a member. CSI also confirmed UCD's calculation of the 5th percentile of the Species Sensitivity Distribution (SSD) using the Burr Type III distribution and the BurrliOZ software. CSI questions the selection of the Burr Type III distribution over the more commonly used log-normal or log-logistic distributions, as implemented in the ETX program. The ETX program is an appropriate tool for describing an SSD; it has the advantages of being well-tested, standardized, and widely accepted throughout the world. Using ETX and the same acute toxicity dataset, CSI calculated an HC5 value for lambda-cyhalothrin of 3.251 ng/L, compared with the HC5 of 2.432 ng/L from BurrliOZ. The Acute Criterion corresponding to the ETX acute value is 2 ng/L, compared with 1 ng/L as derived by UCD.

Methodology: The UCD methodology is generally sound, though some details of the data selection process could be improved. The SSD approach requires data for more species than are typically represented by available guideline studies, and data for additional species generally must be found in non-guideline studies in the open literature. Though data evaluation criteria appropriately favor well-documented GLP guideline studies over non-guideline studies in the open literature, too-stringent criteria will reject useful data and may limit the applicability of the SSD approach.

For derivation of Chronic Criteria, ECx values are preferable to MATCs. An MATC simply reflects a determination of statistical significance, regardless of biological significance or magnitude of effect. An ECx represents a specific magnitude of effect. Appropriate values of *x* have not yet been agreed upon, but they should be selected with biological significance in mind.

Bioavailability: Pyrethroids that are bound to particulate matter or associated with dissolved organic matter are not biologically available to aquatic organisms and do not contribute to toxicity; only freely dissolved pyrethroids are bioavailable and toxic. In laboratory toxicity tests using water with minimal particulate or dissolved organic matter, nearly all the pyrethroid is bioavailable. In ambient water, only a small fraction – a few percent or less – of the total pyrethroid may be bioavailable. Compliance with lambda-cyhalothrin water quality standards should therefore be based on concentrations of freely dissolved lambda-cyhalothrin, not total lambda-cyhalothrin. Freely dissolved lambda-cyhalothrin can be measured directly using solid phase microextraction (SPME), or calculated using an equilibrium partitioning model. Any water quality program should measure or calculate freely dissolved lambda-cyhalothrin concentrations to ensure appropriate comparison to concentrations calculated as Acute or Chronic Criteria.

Mesocosm and Microcosm Data: The mesocosm and microcosm studies summarized in the WQC report, as well as others that were not cited by UCD, indicate that multiple exposures to concentrations of lambda-cyhalothrin much greater than the proposed acute and chronic criteria have no effect, or at most a slight and transient effect, on a variety of aquatic ecosystems. UCD interprets these findings as confirmation that the proposed criteria are sufficiently protective. In fact, the mesocosm/microcosm findings suggest that adequate protection could be achieved with higher criteria.

1. Introduction

As part of the Central Valley Pesticide TMDL and Basin Plan Amendment Project, draft water quality criteria for the pyrethroid insecticide lambda-cyhalothrin have been derived by the University of California, Davis (Fojut and Tjeerdema 2010) and are being circulated for public comment. Compliance Services International (CSI), Lakewood WA, has developed the comments presented below on behalf of Syngenta Crop Protection, Inc., the registrant for lambda-cyhalothrin.

2. Derivation of Acute and Chronic Criteria for Lambda-Cyhalothrin

CSI conducted a thorough examination of the data selected by UCD for derivation of the acute and chronic criteria for lambda-cyhalothrin and found it to be relatively consistent with the data compiled by the Pyrethroid Working Group (PWG), of which Syngenta is a member.

CSI also confirmed UCD's calculation of the 5th percentile (HC5) of the Species Sensitivity Distribution (SSD) using the Burr Type III distribution and the BurrliOZ software. However, CSI questions the selection of the Burr Type III distribution over the more commonly used log-normal or log-logistic distributions, as implemented in the ETX program. The ETX program is an appropriate tool for describing an SSD; it has the advantages of being well-tested, standardized, and widely accepted throughout the world. Using ETX and the same acute toxicity dataset, CSI calculated an HC5 value for lambda-cyhalothrin of 3.251 ng/L, compared with the HC5 of 2.432 ng/L from BurrliOZ. The Acute Criterion corresponding to the ETX acute value is 2 ng/L, compared with 1 ng/L as derived by UCD. The Chronic Criterion (1 ng/L) is unaffected by the choice of SSD models.

3. Comments on UCD Methodology for Deriving Water Quality Criteria

3.1 Data collection

The goal of data collection is stated as "to find virtually all available physical-chemical and ecotoxicity data for a given pesticide" (TenBrook *et al*. 2009, Section 3-2.1). "Only data for freshwater species that are members of families with reproducing populations in North America will be used for criteria derivation, but all data should be collected as it may be used for supporting information or for derivation of an acute-to-chronic ratio (ACR)." This restriction is unnecessary, because toxicity test species are surrogates for all species, and there is no indication that species from North American families are better surrogates than species from families that do not occur in North America.

TenBrook *et al*. (2009, Section 3-2.1) note that "data from agencies [i.e., GLP studies submitted to agencies by registrants] can make up most of the high quality toxicity studies available, especially for compounds with limited data. " We agree with this generalization. The deficiencies of academic studies published in the open literature are generally of two kinds: use of non-standard test protocols, and failure to report data critical to evaluation of study acceptability. This issue is further discussed in Section 3.2 below.

TenBrook *et al*. (2009, Section 3-2.1.1.2) state, "For derivation of chronic criteria or acute-to-chronic ratios, obtain maximum acceptable toxicant concentrations (MATCs). Chronic data expressed as ECx values (from regression analysis), may be used for criteria derivation only if studies are available to show what level of *x* is appropriate to represent a no-effect level." However, use of the MATC does not address the question of determining an appropriate value of *x*; the MATC is based on determinations of statistical significance, regardless of biological significance or magnitude of effect. An MATC can be associated with a wide range of ECx values depending on the nature of the measurement endpoint and the variability of the measurements. We believe it is better to establish (as a matter of policy grounded in science) a tolerable level of effect for a particular species and endpoint, and use concentration-

effect models (e.g., regression analysis) to estimate the concentration corresponding to that level of effect, i.e., the ECx.

3.2 Data evaluation

The UCD methodology calls for an evaluation of the data for relevance first, and for reliability only if the relevance score is 70 or greater. This tiered approach makes data selection more efficient, because a relevance evaluation can usually be done very quickly and no further time needs to be invested in evaluating the reliability of an irrelevant study.

For relevant studies, the recommended process is to extract information to data sheets, and use the results to evaluate reliability according to the rating systems shown in Tables 3.7 and 3.8 of TenBrook *et al*. (2009). While the data extraction process (using the forms provided) can be cumbersome, it is objective and reasonably complete, and does provide a good basis for evaluating data reliability and documenting the evaluation.

Two categories of reliability criteria are used: Documentation and Acceptability. Many criteria in the two groups are related. For example, failure to report dissolved oxygen concentrations results in loss of 4 points for Documentation, and inability to confirm that dissolved oxygen concentrations were acceptable results in loss of 6 points for Acceptability. Thus, a peer-reviewed open-literature publication that fails to report dissolved oxygen concentrations has already lost 10 points (out of 200) in its Reliability score. Failure to report pH, hardness, alkalinity, and conductivity results in loss of 16 more points. These water quality variables are needed only to confirm that the test was run under acceptable conditions – they generally do not affect the outcome of the test – yet their omission from a publication results in a substantially reduced reliability rating.

Similar reporting deficiencies (not uncommon in journal articles, where words are often at a premium) can result in a useful toxicity test receiving a rating of "Less Reliable." In contrast, because of the data reporting requirements for regulatory studies and the requirements of Good Laboratory Practices, studies submitted by registrants are nearly always "Reliable."

An unavoidable consequence of the reliability evaluation is that standard studies, many of which test species that are known to be highly sensitive to pesticides (e.g., daphnids, mysid shrimp, amphipods, and salmonid fish), are more likely to be included in criteria derivation than studies on non-standard species. The use of sensitive species in standard toxicity tests confers additional conservatism on the derived criteria.

3.3 Acute Criterion derivation using SSD

The UCD methodology (TenBrook *et al*. 2009) requires data for at least 5 species representing at least the following 5 groups: the family Salmonidae (e.g. rainbow trout), a warm water fish (e.g. bluegill sunfish, fathead minnow), a planktonic crustacean – at least one from the family Daphniidae (e.g. *Daphnia magna*, *Ceriodaphnia dubia*), a benthic crustacean (e.g., *Hyalella azteca*, *Gammarus pulex*), and an aquatic insect (e.g., *Cloeon dipterum*). UCD's acute dataset for lambda-cyhalothrin, with 20 species, fulfilled all five categories.

TenBrook *et al*. (2009) provide detailed statistical guidance for SSD analysis, but recommend using the BurrliOZ program (CSIRO 2001) or the ETX program (Van Vlaardingen *et al*. 2004) to derive the Acute Criterion. These programs are among the many tools and methods available for estimating the 5th percentile of the SSD. ETX has the advantages of being user-friendly, reliable, standardized, and widely accepted throughout the world.

3.4 Chronic Criterion derivation

Deriving a Chronic Criterion using the SSD approach requires MATC values for at least five species from the same categories as the acute criterion. Reasons for using ECx values rather than MATCs were presented above (Section 3.1).

If chronic data are insufficient for an SSD approach, an ACR approach is used (TenBrook *et al*. 2009, Section 3-4.2). At first, TenBrook *et al*. (2009, Section 3-4.2.1) seem to require that the acute and chronic data used to calculate an ACR must come from the same study in the same dilution water, but then this requirement is relaxed to allow a different study in the same laboratory under identical conditions, or even in a different laboratory – in other words, only the dilution water must be the same. The rationale for this requirement is unclear, since toxicity values are not presumed to be strongly affected by the source of laboratory dilution water.

ACRs are required for three species, including a fish and an invertebrate. If there are insufficient data, a default ACR of 12.4 is used for one or more of these species. The default ACR (TenBrook *et al*. 2009, Section 3-4.2.3) is the 80th percentile value derived from ACRs for 8 insecticides (chlordane, chlorpyrifos, diazinon, dieldrin, endosulfan, endrin, lindane, and parathion). TenBrook *et al*. (2009) do not explain why these insecticides should be considered representative of pesticides from different chemical groups, or why the 80th percentile should be used as the basis for a default ACR. Because ACRs for three species were available for lambda-cyhalothrin, the default ACR was not used in this case.

4. Bioavailability of Lambda-Cyhalothrin

The draft criteria report summarizes evidence that pyrethroids bound to particulate matter are not biologically available to aquatic organisms and do not contribute to toxicity; only freely dissolved pyrethroids are bioavailable and toxic. Bound pyrethroids become bioavailable only when they desorb from particles or dissociate from dissolved organic matter.

The UCD report notes the possibility that pyrethroids can be taken up from ingested particles, citing the findings of Mayer *et al*. (2001) as evidence that hydrophobic compounds can be desorbed by digestive juices. The cited study involved uptake of benzo(a)pyrene and zinc by 18 species of benthic marine invertebrates, including 10 species of worms, 5 species of echinoderms, 2 species of mollusks, and a sea anemone. The relevance of these findings to uptake of pyrethroids by sensitive freshwater taxa (such as insects and crustaceans) is unclear. There is no evidence for uptake of pyrethroids by this route, and the UCD report in fact summarizes the evidence to the contrary.

TenBrook *et al*. (2009, Section 3-5.1) state that when a pesticide has only a single bioavailable phase (sorbed to solids, associated with dissolved organic matter, or freely dissolved in water), it is appropriate to evaluate compliance with water quality standards based on concentrations in the bioavailable phase alone. This is the case for lambda-cyhalothrin and other pyrethroids, of which only the freely dissolved phase is bioavailable. Pyrethroid concentrations in the freely dissolved phase can be measured using techniques such as solid-phase microextraction (SPME), or calculated based on partitioning coefficients (Equation 3.6, TenBrook *et al*. 2009). The equilibrium partitioning model requires input values for dissolved and particulate organic carbon (OC); UCD considers these values to be site-specific properties that are "laborious" to measure. CSI disagrees: measurement of dissolved and particulate organic carbon and total suspended solids is not particularly difficult (compared to analysis of lambda-cyhalothrin, for example) and is useful for calculation of freely dissolved lipophilic chemicals. The US EPA uses equilibrium partitioning models to estimate freely dissolved concentrations of pyrethroids in sediment pore water, based on measured or default values for dissolved and particulate organic carbon concentrations (e.g., USEPA 2005).

In laboratory toxicity tests using low-particulate, low-OC water as the exposure medium, pyrethroids are much more bioavailable than in water with natural levels of particulates and OC. Because aquatic toxicity test guidelines require

the use of water containing minimal amounts of particulate matter and dissolved organic carbon, bioavailability is not a significant factor under standard test conditions. In ambient water, however, analysis of total pyrethroid is liable to overestimate the bioavailable concentration by at least an order of magnitude. For these reasons, we believe that evaluation of water quality compliance for pyrethroids should be based on measured or calculated concentrations of freely dissolved pyrethroid, consistent with the recommendations of TenBrook *et al*. (2009, Section 3-5.1).

We therefore do not concur with UCD's recommendation that criteria compliance be based on whole-water lambda-cyhalothrin concentrations, without consideration of bioavailability. UCD concedes that use of whole-water concentrations is likely to be overprotective, but accepts such overprotection as "compensating for the use of nominal concentrations and unknown effects of dietary exposure." Since the bioavailable fraction may be on the order of a few percent or less of the whole-water lambda-cyhalothrin concentration, the overprotection that would be incurred by basing compliance on whole-water concentrations greatly outweighs the potential underprotection (a factor of 2 or 3 at most) caused by use of nominal concentrations. UCD suggests that this recommendation should be revised when more toxicity data based on measured concentrations are available. We note that measured concentrations are already available for 10 of the 20 relevant and reliable studies in the final database.

5. Mesocosm and Microcosm Data

UCD identified and rated 11 mesocosm and microcosm studies, but only presented results for 8, including 5 rated relevant and reliable and 3 rated less relevant and reliable (Fojut and Tjeerdema 2010, Table 10). The rating forms were not presented. UCD characterized the studies as primarily representing riverine environments, but in fact only 2 of the 8 (both rated less reliable) involved flowing water.

An important study not cited in the UCD report was the GLP guideline study by Hill et al. (1994a,b). In this study, large outdoor ponds were treated with 12 simulated spray drift events at weekly intervals and 6 simulated runoff events at two-week intervals, using three treatment rates. The lowest spray treatment rate corresponded to a nominal concentration of 1.7 ng/L (from each of the 12 applications), and the lowest runoff treatment rate corresponded to a nominal concentration of 5 ng/L; the other treatment rates were 10 and 100 times greater than the lowest rate. Results were similar to those obtained by Farmer et al. (1995), with minor and transient effects on invertebrates at the low and medium treatment rates. No adverse effects on fish were observed in any of the treatments.

The mesocosm and microcosm studies summarized by UCD, as well as the study by Hill et al. (1994a,b), indicate that multiple exposures to concentrations much greater than the proposed acute and chronic criteria have no effect, or at most a slight and transient effect, on a variety of aquatic ecosystems. UCD interprets these findings as confirmation that the proposed criteria are sufficiently protective. In fact, the mesocosm/microcosm findings suggest that adequate protection could be achieved with higher criteria.

6. Conclusions

- The UCD methodology for deriving numeric water quality criteria (TenBrook *et al*. 2009) is generally sound, though some details of the data selection process could be improved. The SSD approach requires data for more species than are typically represented by available guideline studies, and data for additional species generally must be found in non-guideline studies in the open literature. Though data evaluation criteria appropriately favor well-documented GLP guideline studies over non-guideline studies in the open literature, too-stringent criteria will reject useful data and may limit the applicability of the SSD approach.

- For derivation of Chronic Criteria, ECx values are preferable to MATCs. An MATC simply reflects a determination of statistical significance, regardless of biological significance or magnitude of

effect. An ECx represents a specific magnitude of effect. Appropriate values of *x* have not yet been agreed upon, but they should be selected with biological significance in mind.

- Pyrethroids bound to particulate matter or associated with dissolved organic matter are not biologically available to aquatic organisms and do not contribute to toxicity; only freely dissolved pyrethroids are bioavailable and toxic. In laboratory toxicity tests using water with minimal particulate or dissolved organic matter, nearly all the pyrethroid is bioavailable. In natural water, only a small fraction – a few percent or less – of the total pyrethroid may be bioavailable. Compliance with lambda-cyhalothrin water quality standards should therefore be based on concentrations of freely dissolved lambda-cyhalothrin, not total lambda-cyhalothrin. Freely dissolved lambda-cyhalothrin can be measured directly using solid phase microextraction (SPME), or estimated using an equilibrium partitioning model such as the one presented by Tenbrook *et al*. (2009).

- The mesocosm and microcosm studies summarized by UCD, as well as others that were not included in this document, indicate that multiple exposures to concentrations much greater than the proposed acute and chronic criteria have no effect, or at most a slight and transient effect, on a variety of aquatic ecosystems. UCD interprets these findings as confirmation that the proposed criteria are sufficiently protective. In fact, the mesocosm/microcosm findings suggest that adequate protection could be achieved with higher criteria.

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